PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-251779

(43)Date of publication of application : 09.09.1994

(51)Int.Cl. H01M 8/02
H01M 8/10

(21)Application number : 05-035241

(22)Date of filing : 24.02.1993

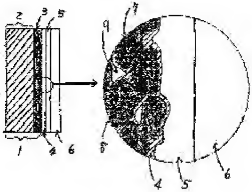
(71)Applicant : ASAHI CHEM IND CO LTD

(72)Inventor : NOAKI YASUHIDE
OKAMOTO SABURO

(54) FORMATION OF JOINED BODY OF SOLID POLYMER ELECTROLYTE LAYER AND ELECTRODE FOR FUEL CELL

(57)Abstract:

PURPOSE: To provide a forming method of a joined body having low electric resistance such as a joined interface or a solid polymer electrolyte layer by which formation becomes simple by forming the first layer by heat treatment after fluorine type polymer solution is applied and dried on the side surface having electrode catalyst.



CONSTITUTION: When a joined body is formed, after fluorine type polymer solution being a polymer electrolyte is applied and dried on the surface of an electrode catalyst layer 3 of a gas diffusing electrode 1, the first layer 4 of solid polymer electrolyte is formed by heat treatment. The second layer 5 and the third layer 6 of solid polymer electrolyte are formed by applying fluorine type polymer solution on the first layer 4. An electrode catalyst layer 3 has a pore 9, and gas is supplied to an electrode catalyst particulate 8 by this pore 9. Thereby, the first electrolyte layer 4 requires a thickness in a degree that the pore 9 is not blocked and a gas flow is not hindered, and when the solution is applied on and after the second electrolyte layer 5, a phenomenon that the first layer 4 is dissolved or this pore is reduced or belocked up can be prevented by a method in the present invention.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号

特開平6－251779

(43)公開日　平成6年(1994) 9月9日

(51)Int.Cl.5		識別記号	庁内整理番号	FI	技術表示箇所
H01M	8/02	E	8821－4K		
	8/10		8821－4K		

審査請求　未請求　請求項の数1　OL　（全 6 頁）

(21)出願番号　特願平5－35241

(22)出願日　平成5年(1993) 2月24日

(71)出願人　000000033
旭化成工業株式会社
大阪府大阪市北区堂島浜1丁目2番6号

(72)発明者　野秋　康秀
宮崎県延岡市旭町6丁目4100番地　旭化成工業株式会社内

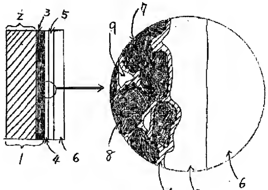
(72)発明者　岡本　三郎
宮崎県延岡市旭町6丁目4100番地　旭化成工業株式会社内

(54)【発明の名称】　燃料電池用固体高分子電解質層と電極との接合体の作成方法

(57)【要約】

【目的】　製作が簡単で接合界面や固体高分子電解質層の電気抵抗、物質移動抵抗が小さい密着性のすぐれた燃料電池用固体高分子電解質と電極の接合体の製作方法を提供することにある。

【構成】　燃料電池用固体高分子電解質と電極との接合体を製作する際、電極上に高分子電解質となるをフッ素系ポリマーの溶液を電極触媒を有する側に塗布し乾燥させた後、熱処理することにより第一層を形成し、更に第一層上にスルホン酸基を含むフッ素系ポリマー溶液を塗布することにより、第二層以降の層を形成する燃料電池用固体高分子電解質と電極との接合体の製作方法。



【特許請求の範囲】

【請求項１】　燃料電池用固体高分子電解質層と電極との接合体を作成するに際し、該電極の電極触媒を有する側表面に高分子電解質となるスルホン酸基を含むフッ素系ポリマーの溶液を塗布し乾燥させた後、熱処理することにより第一層を形成し、更に該第一層上に、スルホン酸基を含むフッ素系ポリマー溶液を塗布し乾燥させた後、熱処理する工程を少なくとも１回行うことにより、第二層以降の層を形成することを特徴とする燃料電池用固体高分子電解質層と電極との接合体の作成方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、燃料電池を構成する燃料電池用固体高分子電解質と電極との接合体の作成方法に関する。

【０００２】

【従来の技術】燃料電池用固体高分子電解質層と電極との接合体として必要な要素の中で特に重要なことは、電極と固体高分子電解質との接合面での電気抵抗が低いこと、固体高分子電解質自身の電気抵抗が低いこと、高分子電解質が過剰なガス透過性を有しないこと、長期間の使用に対して化学的耐久性や安定性に優れていること及び物理的な強度が強いこと等が上げられる。

【０００３】上記の要素の中で現在特に問題となっているのは、燃料電池用固体高分子電解質自体の電気抵抗がまだ高く燃料電池出力ロスの大きな部分を占めている事である。近年、燃料電池はクリーンな電気エネルギー供給源として注目されており、特にその中で、燃料電池用固体高分子電解質層としてイオン交換膜を用いた固体高分子電解質燃料電池は、作動温度が１００℃以下と低くても、そのエネルギー密度が高いことから、移動用の電源として例えば電気自動車の電源や、簡易補助電源等として期待されている。

【０００４】固体高分子電解質燃料電池は、一般に固体高分子電解質を膜状に成形したいわゆるイオン交換膜をはさんでその両側に電極が接合されており、ガス拡散電極の一方には燃料（例えば水素）が供給され、もう一方には酸化体（例えば酸素又は空気）が供給されることにより電極反応を生ずる構造になっている。燃料電池内では、電極触媒により、供給された燃料が酸化されプロトン即ち水素イオンを発生し、イオン交換膜内をイオン伝導によりもう一方の電極に到達し、酸化体により水を生成する反応が起こっている。

【０００５】イオン交換膜は燃料電池の電極と密接に接合されており、実質的に電極と一体構造に形成されて用いられている。したがって、イオン交換膜は燃料電池内において、水素イオンを伝導するための電解質としての役割と、燃料と酸化体が加圧下においても直接混合しないための隔膜としての役割の両方を備える必要がある。

【０００６】このような燃料電池に用いられるイオン交換膜は、ポリマー主鎖に化学的に結合した複数の酸官能基を備えたプロトン交換型ポリマーフィルムであり、例えばスルホン化ポリスチレンであってもよく、実質的にフッ素化されたスルホン酸ポリマーであっても良い。しかし耐久性の面から、フッ素化されたスルホン酸ポリマーが使われる場合が多い。

【０００７】しかし、現状ではまだ実用的な電極とイオン交換膜との接合方法は確立されておらず、そのため性能も一定していない。更に、イオン交換膜自体の電気抵抗も十分低いとは言えず燃料電池出力のロスの大きな原因ともなっている。現在用いられている燃料電池用のフッ素系のイオン交換膜は、イオン交換膜法クロルアルカリ電解で大量に使用されているものとポリマー構造は類似のものであり、例えばデュポン社製のナフィオン（登録商標）等の酸型のものがよく用いられている。しかしイオン交換膜は、一般的には１００μｍ以上の厚みがあり、電気抵抗を低減するために厚みを小さくしようとしても、膜を製造する際に大きな困難が伴う他、使用する際にも強度が弱くなる等の不都合が生じる傾向があった。

【０００８】イオン交換膜の抵抗を低くしようとすれば、最も簡単な方法としてイオン交換膜の厚みを薄くすることである。しかしイオン交換膜の厚みは製造上限界があることや、厚みを薄くすることによって強度が低下し、電極との接合の際破損する等の問題が生じる危険性が有った。又現在、イオン交換膜とガス拡散電極を接合する際には、あらかじめイオン交換膜と類似のイオン交換樹脂成分の溶液を電極の触媒面に一定量塗布し乾燥させた上で熱プレスにより一体に接合している。イオン交換樹脂成分の溶液は、例えばデュポン社製のナフィオン（登録商標）等の酸型のイオン交換樹脂を水とプロパノールやエチルアルコールと言った水と混合可能な有機溶剤の混合液に約５％溶解したものがよく用いられている。

【０００９】しかし、ガス拡散電極にイオン交換樹脂成分を含んだ溶液を塗布する際の、塗布量や、イオン交換樹脂成分を含んだ溶液の粘度や濃度、皮膜を形成する際の乾燥条件等により、電極とイオン交換膜の接合体の燃料電池作動時の性能にバラツキが生じやすく再現性のある結果は得にくい状況にある。以上の点から、密着性に優れた電気抵抗の低い燃料電池用固体高分子電解質と電極の接合体を製作することは非常に難しかった。

【００１０】特開平４－２６４３６７号公報に提案されている燃料電池では、固体高分子電解質型燃料電池におけるイオン交換膜の薄膜化を可能にし、電気抵抗を低減しようとしている。しかしこの公報に開示されている方法でもまだ不十分であり、また実際には電極触媒層に多量に固体高分子電解質成分がしみこみ、電極の細孔を閉塞して性能を低下させたり、固体高分子電解質層の厚みを制御しにくい等の問題点もあった。

【００１１】

【発明が解決しようとする課題】本発明は、燃料電池用のガス拡散電極と固体高分子電解質との接合体を作成する際、作成が簡単で、かつ接合界面や固体高分子電解質層の電気抵抗の低い燃料電池用固体高分子電解質と電極の接合体の作成方法を提供することを目的とする。

【００１２】

【課題を解決するための手段】本発明者等は製作しやすく電極とイオン交換膜との密着性の優れた電気抵抗の低い接合体を製作する方法を種々検討した結果、本発明を完成させたものである。すなわち、本発明は、燃料電池用固体高分子電解質層と電極との接合体を作成するに際し、該電極の電極触媒を有する側表面に高分子電解質となるスルホン酸基を含むフッ素系ポリマーの溶液を塗布し乾燥させた後、熱処理することにより第一層を形成し、更に該第一層上に、スルホン酸基を含むフッ素系ポリマー溶液を塗布し乾燥させた後、熱処理する工程を少なくとも１回行うことにより、第二層以降の層を形成することを特徴とする燃料電池用固体高分子電解質層と電極との接合体の作成方法である。

【００１３】燃料電池は、電池に供給される燃料の酸化により化学的エネルギーを直接電気エネルギーに変換する電気化学装置であり、その構造によりいくつかの種類があるが、本発明が利用できるのは、電解質として固体高分子電解質、特にフッ素系プロトン交換型樹脂層を有する燃料電池である。燃料電池に用いられるガス拡散電極は、ガスが透過可能な微細孔を有しており、一般的には活性炭のようなカーボン粒子に微細な白金粒子を担持させたものと、テトラフルオロエチレン粉末を混合し熱プレス成形したものが用いられている。このタイプのガス拡散電極のとしてＥ－ＴＥＫ社製の電極が多く使用されている。

【００１４】本発明においては、まずガス拡散電極の触媒層上にスルホン酸基を含むフッ素系ポリマーの溶液を塗布し１００℃以下で乾燥させ、十分に溶媒が蒸発し乾燥した後に１２０℃以上で熱処理をすることにより第一層を形成し、第一層上に再度スルホン酸基を含むフッ素系ポリマー（以下、イオン交換樹脂成分という。）の溶液で第二層を塗布し乾燥させる。このようにすると第二層を塗布しても塗布溶液が電極内部にしみ込まず必要な厚みの塗膜が得られるのである。

【００１５】ガス拡散電極の触媒層上にイオン交換樹脂成分の溶液を塗布すると、その溶液は電極内にしみ込んでゆく。その際電極内の細孔中の触媒は溶液で覆われその結果乾燥後には触媒表面は電解質でもあるイオン交換樹脂成分の薄膜に覆われることになる。しかし、あまり塗布する溶液の量が多すぎると、電極内の細孔をイオン交換樹脂成分で塞いでしまい、ガスの透過が阻害され、逆に少な過ぎると、触媒粒子の表面に電解質がなく電極反応が進行しなくなる。したがって適度な量のイオン交換樹脂成分が電極触媒層には必要である。

【００１６】このため従来は、電極触媒層上塗布する最適な量を経験的に決めておき、あらかじめその量を塗布しておいて、イオン交換膜と接合する方法をとらざるを得なかった。しかし本発明の場合は、第一層を１２０℃以上の温度で熱処理しているので、第一層上に新たにイオン交換樹脂成分を含む溶液を塗布しても電極内部までしみ込まず、第二層は任意の厚みで塗布することができる利点がある。第二層以降は従来の概念で言えばイオン交換膜に相当する部分でありこの部分の厚みを任意にコントロールできると、イオン交換膜を事実上どのような厚みにでもできることを意味する。したがって、イオン交換膜の抵抗を低下させることや、その他燃料電池にとっては重要な要素となっているイオン交換膜内の水分の拡散量もある程度制御できることにもなる。

【００１７】本発明において、第一層の乾燥温度としてはイオン交換樹脂成分の溶媒があまり急速に蒸発しない程度の温度が望ましい。そのためには１００℃以下２０℃以上であることが好ましく、更に好ましくは８０℃以下、特に好ましくは６０℃以下で乾燥することである。又、第一層目のイオン交換樹脂層を塗布して乾燥したのち、熱処理する場合の温度は１２０℃以上が好ましく、更に好ましくは１３０℃以上、特に好ましくは１４０℃以上が適当である。このような温度で処理しなければならない理由は明確ではないが、塗布し乾燥されたイオン交換樹脂層は、まだポリマー分子どうしの配列がみだれており、ポリマーを溶解しうる溶媒があれば非常に溶解しやすい構造となっているのに対し、１２０℃以上の高温で処理すると熱の影響でポリマーどうしが複雑にからみあい容易には溶媒に溶けない状態に変わるものと推定している。

【００１８】熱処理する際の温度の上限は、事実上ポリマーが変質することがなければどんな温度でもよいが、実際には２５０℃以下、好ましくは２００℃以下がポリマーに影響を与えることが少ないので望ましい。第一層の厚みは、ガス拡散電極の種類によっても異なるので経験的に決められる場合が多い。又、溶液が電極内にしみ込むため、厚みとして一義的に決められない面もある。しかし、電極触媒にガスの拡散が十分になされる厚みである必要があり、通常は電極触媒表面で５μｍ以下、好ましくは１μｍ以下であることが望ましい。

【００１９】第二層以降を塗布する場合、単純に第一層上にイオン交換樹脂成分を含む溶液を塗布するだけでもよい。しかし、任意の厚みを塗布しようとする場合、何度も塗り重ねる必要がある。その場合、第一層上に一定量の溶液を塗布し１００℃以下で乾燥させ、次に１２０℃以上で熱処理した後、更にその上に同様な方法で塗り重ねてゆき、第二層以降が任意の厚みになるまで繰り返す方法が好ましい。又第二層以降は、第一層と異なる交換容量を持つイオン交換樹脂成分を塗布することもでき

る。

【0020】第一層以外の厚みは、イオン交換樹脂層の電気抵抗を削減する意味では薄ければ薄い程良いが、燃料電池を構成する際の強度面や、通電時に電極どうしがショートする危険がないようにすること等を考慮して決定する必要がある。このようなことに配慮した場合、第二層以降の合計厚みとしては、5μm以上は必要であり、10μm以上が更に好ましい。

【0021】本発明に用いられる、イオン交換樹脂成分を含む溶液としては、フッ素系イオン交換樹脂成分を含むものであれば何でもよいが、例えば次の化学式を持つポリマーであることが好ましい。

【0022】

【化1】

$$-[(CF_2-CF_2)_i-(CF_2-\underset{\substack{|\\(OCF_2-\underset{\substack{|\\CF_3}}{CF})_x-O-(CF_2)_y-SO_3H}}{CF})_j]_n-$$

(式中x=0～2;y=2～3;i/j=0～10)

【0023】イオン交換樹脂成分の当量重量は、電気抵抗面からは小さい程良いが、余りに小さすぎると強度が弱くなる等の問題があるので、実用的には1100g/eq～600g/eqが好ましい。イオン交換樹脂成分を含む溶液の溶媒は、特に限定されないが、例えばイソプロパノール、プロパノール、エタノール、メタノール等に水を加えた混合溶媒を用いることができる。

【0024】図1は本発明の接合体を模式化して示したものである。図1において、ガス拡散電極1は、疎水化層2と電極触媒層3からなっており、電極触媒層3の内部から表面までに固体高分子電解質層第一層4が形成されている。固体高分子電解質層第一層4上には固体高分子電解質層第二層5が形成され、更にその上に固体高分子層第三層6が形成されている。電極触媒層3にはカーボン7上に担持された電極触媒微粒子8があり、その上に固体高分子電解質層第一層4がコーティングされている。

【0025】固体高分子層第一層は、電極触媒層3内に一部がしみこみ電極触媒微粒子8が担持されたカーボン7上も覆っている。電極触媒層3には空孔9があり、この空孔9によりガスが電極触媒8に供給される。固体高分子電解質層第一層4は、電極触媒層3内にある空孔9を閉塞しガスの流通を阻害しない程度の厚さである必要がある。このため、固体高分子電解質層第二層以降を塗布する際は、固体高分子電解質層第一層が再度溶解したり或は第一層を通して固体高分子電解質成分がしみこみ、この空孔を小さくしたり閉塞しないようにすることが肝心である。本発明の方法により第一層を形成すると、このようなことは起こらないので高性能な燃料電池を構成できる。

【0026】図1のような固体高分子電解質層と電極との接合体を用いて燃料電池を構成する際には、二層以上の固体高分子電解質層を有する電極ともう一方は第一層のみを有する電極とを、固体高分子電解質の層を有する側どうしを密着させ、熱プレス接合する方法や、二層以上の固体高分子電解質層を持つ電極どうしを同様に接合する方法が好ましい。一方の電極には二層以上の固体高分子電解質層を有する電極とこのような層を持たない電極との接合は、電極との密着性が悪くなり、電気抵抗が高くなる傾向があり好ましくない。

【0027】固体高分子電解質層を有する電極を接合する際の温度は、固体高分子電解質がある程度やわらかくなる温度であることが好ましく、通常120℃以上、良好な接着を得るには140℃以上が好ましい。接合する際の圧力は、接合温度に対し良好な接着の得やすい圧力に決めればよく、特に限定されない。このようにして、本発明の作成方法で得られた固体高分子電解質層と電極との接合体を用いて燃料電池を構成し、酸素ガス及び水素ガスを原料に電気を取り出すと、従来の電極とイオン交換膜接合体を用いた場合より高い燃料電池出力が得られ、その安定性も従来のものと変わらない。

【0028】かくして、本発明は燃料電池用固体高分子電解質と電極との接合体を作成する際、電極上に高分子電解質となる層をスルホン酸基を含むフッ素系ポリマーの溶液を電極触媒を有する側に塗布し熱処理することにより第一層を形成し、更に第一層上にスルホン酸基を含むフッ素系ポリマー溶液を塗布することにより、第二層以降の層を形成させることにより形成されるので、固体高分子電解質の層を薄くでき、接合界面や固体高分子電解質層の電気抵抗、物質移動抵抗が小さい密着性のすぐれており、出力の大きい燃料電池を構成できる。

【0029】次に本発明を実施例により説明するが、これに限定されるものではない。

【0030】

【実施例】

【0031】

【実施例1】下記化2に示される当量重量1000g／eqの固体高分子電解質であるイオン交換樹脂成分5重量%を含む溶液Aを準備した。

【0032】

【化2】

$$-\left[(CF_2-CF_2)_i-(CF_2-CF)_j\right]_n-$$

$$\begin{array}{l} \quad | \\ OCF_2-CF-O-(CF_2)_2-SO_3H \\ \qquad\;\; | \\ \qquad\; CF_3 \end{array}$$

（iは当量重量に見合う値）

【0033】溶液Aの組成は、プロピルアルコール85部、水10部、イオン交換樹脂成分5部を含むものとした。燃料電池用ガス拡散電極としては、サイズ3cm×3cmのE－TEK社製で白金触媒が0．35mg／cm^2 であるもの2枚を準備した。この2枚の電極の触媒面に、溶液Aを117mgづつ塗布し40℃の温度で約1時間乾燥させた。その後さらに温度140℃の熱風乾燥機内で10分間熱処理し、第一層を形成した。第一層を形成させた後、二枚の電極の第一層上に、117mgの溶液Aを塗布し、40℃で1時間乾燥させ、更に140℃の熱風乾燥機内で10分間熱処理し第二層を形成させた。第二層を形成させた後、第三層、第四層、第五層迄を第二層と同様な方法で形成した。

【0034】次に、この二枚の電極の塗布層側どうしを密着させ熱プレス装置で、145℃、60kg／cm^2 の条件で90秒間熱プレスし、接合体Bを得た。このようにして作成された接合体Bは、固体高分子電解質層の厚みは約20μmで、接合状態も強固で簡単に剥離しなかった。この接合体Bをその両側に電気を取り出すための給電体を密着させてガスの取り入れ口及び抜き出し口がある内寸2cm×2cm、外寸3cm×3cmフランジの間に装着して燃料電池本体を構成した。燃料電池を外部負荷に接続し、一方に水素ガス、もう一方に酸素ガスを供給しつつ55℃、1atmの条件で出力電流と出力電圧を測定した。その結果を図2に示す。

【0035】

【比較例1】実施例1と全く同様の溶液A及びガス拡散電極を準備した。又イオン交換膜としてフッ素系のスルホン酸型のイオン交換膜であるDuPont社のナフィオン117も合わせて準備した。実施例1と同一の電極二枚を準備し、140℃で熱処理を行なわない以外は実施例1と全く同様な条件で第一層を形成した。

【0036】イオン交換膜は、あらかじめ8%硫酸2時間100℃で処理し、その後純水で洗浄したのち約1時間沸騰した純水中に浸漬しておいた。イオン交換膜の表面の水滴をふきとった後、二枚の電極の塗布面をイオン交換膜側に向けて密着させ、熱プレス装置で、145℃、60kg／cm^2 の条件で90秒間熱プレスし、接合体Cを得た。

【0037】この接合体Cを実施例1と全く同様に、燃料電池を構成して性能を測定した。結果を図2に示す。本発明方法で作成された燃料電池用固体高分子電解質層と電極との接合体は、燃料電池性能が良いことが明白である。

【0038】

【発明の効果】本発明の製作方法によって、燃料電池用固体高分子電解質と電極との接合体を製作する際、固体高分子電解質層を薄く形成できるので、固体高分子電解質層の電気抵抗、物質移動抵抗が小さい密着性のすぐれた、出力の大きい燃料電池を構成できる。

【図面の簡単な説明】

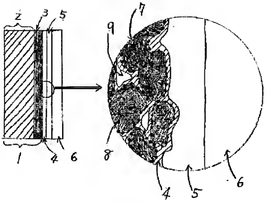
【図1】本発明の固体高分子電解質と電極との接合体を模式化して示した断面図、及びその部分拡大図である。

【図2】本発明の実施例1及び比較例1の固体高分子電解質燃料電池の出力電流と出力電圧の特性を示したグラフ図である。

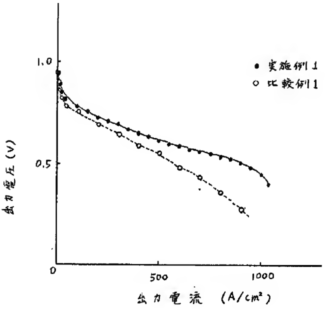
【符号の説明】

1　ガス拡散電極
2　疎水化層
3　電極触媒層
4　固体高分子電解質層第一層
5　固体高分子電解質層第二層
6　固体高分子電解質層第三層
7　カーボン
8　電極触媒微粒子
9　空孔

【図１】



【図２】



CLAIMS

[Claim(s)]
[Claim 1] It faces creating the zygote of the solid-state polyelectrolyte layer for fuel cells, and an electrode. After making the side front face which has the electrode catalyst of this electrode apply and dry the solution of the fluorine system polymer containing the sulfonic group used as a polyelectrolyte, By forming the first pass by heat-treating, and performing the process to heat-treat once [at least] further, after applying and drying the fluorine system polymer solution which contains a sulfonic group on this first pass The creation approach of the zygote of the solid-state polyelectrolyte layer for fuel cells and electrode which are characterized by forming the layer after the second layer.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the creation approach of the zygote of the solid-state polyelectrolyte for fuel cells and electrode which constitute a fuel cell.
[0002]
[Description of the Prior Art] It is raised that that it is important especially in an element required as a zygote of the solid-state polyelectrolyte layer for fuel cells and an electrode has the low electric resistance in the plane of composition of an electrode and a solid-state polyelectrolyte, that own electric resistance of a solid-state polyelectrolyte is low, not having gas permeability with a superfluous polyelectrolyte, excelling in chemical durability or stability to prolonged use, that physical reinforcement is strong, etc.
[0003] It poses current, especially a problem in the above-mentioned element that the electric resistance of the solid-state polyelectrolyte for fuel cells itself still occupies the high, big part of a fuel cell output loss. In recent years, the fuel cell attracts attention as a clean electrical energy source of supply, and since the energy density is high even if operating temperature is as low as 100 degrees C or less, the using ion exchange membrane as solid-state polyelectrolyte layer for fuel cells especially solid-state polyelectrolyte fuel cell in it is expected as the power source of an electric vehicle, simple auxiliary power, etc. as a power source for migration.
[0004] The solid-state polyelectrolyte fuel cell has structure which produces electrode reaction by joining the electrode to the both sides on both sides of the so-called ion exchange membrane which fabricated the solid-state polyelectrolyte in the shape of film generally, supplying a fuel (for example, hydrogen) to one side of a gas diffusion electrode, and supplying an oxidant (for example, oxygen or air) to another side. Within the fuel cell, the supplied fuel oxidized according to the electrode catalyst, the proton, i.e., a hydrogen ion, was generated, another electrode was reached according to ionic conduction in the inside of ion exchange membrane, and the reaction which generates water with an oxidant has occurred.
[0005] It is closely joined to the electrode of a fuel cell, and ion exchange membrane is substantially formed in an electrode and integral construction, and is used. Therefore, ion exchange membrane needs to be equipped with both a role of an electrolyte for conducting a hydrogen ion in a fuel cell, and a role of a diaphragm not to mix a fuel and an oxidant directly under pressurization.
[0006] The ion exchange membrane used for such a fuel cell may be the proton exchange mold polymer film equipped with two or more acid functional groups chemically combined with the polymer principal chain, for example, may be sulfonated polystyrene, and may be the sulfonic-acid polymer fluorinated substantially. However, from the field of endurance, the fluorinated sulfonic-acid polymer is used in many cases.

[0007] However, in the present condition, it is not established, therefore the junction approach of of a still practical electrode and ion exchange membrane does not fix the engine performance, either. Furthermore, the electric resistance of the ion exchange membrane itself cannot be referred to as sufficiently low, either, but has also become the big cause of the loss of a fuel cell output. The thing and polymer structure where the ion exchange membrane of the fluorine system for fuel cells used now is used in large quantities by ion exchange membrane process KURORU alkali electrolysis are a like, for example, the acids [, such as Du Pont Nafion (trademark),] type thing is used well. However, generally ion exchange membrane had the thickness of 100 micrometers or more, in order to reduce electric resistance, even if it was going to make thickness small, when manufacturing the film, big difficulty followed, and also when using it, it had the inclination which un-arranging -- reinforcement becomes weak -- produces.
[0008] If it is going to make resistance of ion exchange membrane low, it will be making thickness of ion exchange membrane thin as easiest approach. However, reinforcement fell that there is a manufacture upper limit community and by making thickness thin, and the thickness of ion exchange membrane had the danger that the problem of damaging in case it is junction to an electrode would arise. Moreover, in case a gas diffusion electrode is joined to current and ion exchange membrane, after carrying out constant-rate spreading and making the catalyst side of an electrode dry the solution of an ion-exchange-resin component similar to ion exchange membrane beforehand, it has joined to one with a heat press. What the solution of an ion-exchange resin component dissolved in the mixed liquor of water and a mixable organic solvent which said acids [, such as Du Pont Nafion (trademark),] type ion-exchange resin as water, and propanol and ethyl alcohol about 5% is used well.
[0009] However, the result which has repeatability in the engine performance at the time of fuel cell actuation of an electrode and the zygote of an ion exchange membrane that it is easy to produce variation according to the desiccation conditions at the time of forming the viscosity and concentration of the solution containing the coverage and the ion-exchange-resin component at the time of applying the solution which contained the ion-exchange-resin component in the gas diffusion electrode, and a coat etc. is in the situation which is hard to acquire. It was very difficult to manufacture the zygote of the solid-state polyelectrolyte for fuel cells with low electric resistance, and an electrode excellent in adhesion from the above point.
[0010] In the fuel cell proposed by JP,4-264367,A, thin film-ization of the ion exchange membrane in a solid-state polyelectrolyte mold fuel cell tends to be enabled, and it is going to reduce electric resistance. However, still insufficiently [the approach currently indicated by this official report], the solid-state polyelectrolyte component sank into the electrode catalyst bed so much in fact, the pore of an electrode was blockaded, the engine performance was reduced and there was also a trouble of being hard to control the thickness of a solid-state polyelectrolyte layer.
[0011]
[Problem(s) to be Solved by the Invention] In case this invention creates the zygote of the gas diffusion electrode for fuel cells, and a solid-state polyelectrolyte, it aims at creation offering the creation approach of the zygote of the easy solid-state polyelectrolyte for fuel cells with the low electric resistance of a junction interface or a solid-state polyelectrolyte layer, and an electrode.
[0012]
[Means for Solving the Problem] this invention person etc. completes this invention, as a result of examining various the approaches of manufacturing a zygote with the low electric resistance which was [that it is easy to manufacture] excellent in the adhesion of an electrode and ion

exchange membrane. Namely, this invention is faced creating the zygote of the solid-state polyelectrolyte layer for fuel cells, and an electrode. After making the side front face which has the electrode catalyst of this electrode apply and dry the solution of the fluorine system polymer containing the sulfonic group used as a polyelectrolyte, By forming the first pass by heat-treating, and performing the process to heat-treat once [at least] further, after applying and drying the fluorine system polymer solution which contains a sulfonic group on this first pass It is the creation approach of the zygote of the solid-state polyelectrolyte layer for fuel cells and electrode which are characterized by forming the layer after the second layer.

[0013] A fuel cell is electrochemistry equipment which transforms a chemical energy into direct electrical energy by oxidation of the fuel supplied to a cell, and although there are some classes according to the structure, the fuel cell which has a solid-state polyelectrolyte, especially a fluorine system proton exchange mold resin layer as an electrolyte can use this invention. The gas diffusion electrode used for a fuel cell has the micropore which can penetrate gas, and the thing which made a carbon particle like activated carbon support a detailed platinum particle generally, and the thing which mixed and carried out heat press forming of the tetrafluoroethylene powder are used. Many electrodes made from E-TEK are used as that of this type of gas diffusion electrode.

[0014] After applying the solution of the fluorine system polymer which contains a sulfonic group on the catalyst bed of a gas diffusion electrode first in this invention, making it dry below 100 degrees C and a solvent's fully evaporating and drying, the first pass is formed, and the second layer is applied and it is made to dry on the first pass by heat-treating above 120 degrees C with the solution of the fluorine system polymer (henceforth an ion-exchange-resin component) which contains a sulfonic group again. If it does in this way, even if it will apply the second layer, a spreading solution does not sink into the interior of an electrode, but the paint film of required thickness is obtained.

[0015] If the solution of an ion-exchange-resin component is applied on the catalyst bed of a gas diffusion electrode, the solution will sink in in an electrode and will die. The catalyst in the pore in an electrode will be covered with a solution in that case, and, as a result, a catalyst front face will be covered with the thin film of the ion-exchange-resin component which is also an electrolyte after desiccation. However, if there are too many amounts of the solution to apply, an ion-exchange-resin component will close the pore in an electrode, transparency of gas will be checked, if too conversely few, there will be no electrolyte in the front face of a catalyst particle, and electrode reaction will seldom advance. Therefore, a moderate quantity of an ion-exchange-resin component is required for an electrode catalyst bed.

[0016] For this reason, conventionally the optimal amount which carries out electrode catalyst bed glazing cloth is decided experientially, that amount is applied beforehand, and the approach of joining to ion exchange membrane had to be taken. However, since the first pass is heat-treated at the temperature of 120 degrees C or more in the case of this invention, even if it applies the solution which newly contains an ion-exchange-resin component on the first pass, it does not sink in to the interior of an electrode, but the second layer has the advantage which can be applied by the thickness of arbitration. After the second layer, if it says with the conventional concept, and it is a part equivalent to ion exchange membrane and the thickness of this part can be controlled to arbitration, it means that ion exchange membrane is made to any thickness as a matter of fact. Therefore, in addition to this, it is reducing resistance of ion exchange membrane, and controllable [the diffusing capacity of the moisture in the ion exchange membrane used as an important element / to some extent] for a fuel cell.

[0017] In this invention, the temperature whose solvent of an ion-exchange-resin component is extent which does not evaporate not much quickly as a drying temperature of the first pass is desirable. It is that it dries especially preferably below 60 degrees C that it is [100 degree-C or less / 80 degrees C or less] 20 degrees C or more desirable still more preferably for that purpose. Moreover, after applying the ion-exchange-resin layer of a first pass eye and drying, 120 degrees C or more are desirable still more desirable, and 140 degrees C or more 130 degrees C or more are especially preferably suitable for the temperature in the case of heat-treating. if the ion-exchange-resin layer applied and dried although the reason which must process at such temperature is not clear has the solvent which the array of polymer molecules saw, is still dull, and may dissolve a polymer and it will process at an elevated temperature 120 degrees C or more to having the structure which is very easy dissolving, it will presume to be what changes to the condition polymers become entangled intricately under the effect of heat, and do not melt into a solvent easily.
[0018] As long as a polymer does not deteriorate as a matter of fact, what kind of temperature is sufficient as the upper limit of the temperature at the time of heat-treating, but in fact, 250 degrees C or less, since it is rare for 200 degrees C or less to affect a polymer preferably, it is desirable. Since it changes also with classes of gas diffusion electrode, the thickness of the first pass is decided experientially in many cases. Moreover, since a solution sinks in in an electrode, there is also a field which is not uniquely decided as thickness. However, it is necessary to be the thickness by which diffusion of gas is fully made by the electrode catalyst, and it is usually desirable on an electrode catalyst front face that it is 1 micrometer or less preferably 5 micrometers or less.
[0019] When applying the second layer or subsequent ones, it is also simply good on the first pass to apply the solution containing an ion-exchange-resin component. However, when it is going to apply the thickness of arbitration, it is necessary to recoat repeatedly. In that case, after applying the solution of a constant rate on the first pass, making it dry below 100 degrees C and then heat-treating above 120 degrees C, the approach of repeating until it recoats by the still more nearly same approach on it and the second layer or subsequent ones becomes the thickness of arbitration is desirable. After two layer of ****, an ion-exchange-resin component with different exchange capacity from the first pass can also be applied.
[0020] In the semantics which reduces the electric resistance of an ion-exchange-resin layer, although it is better as thin, it is necessary to determine thickness other than the first pass in consideration of making it the side on the strength at the time of constituting a fuel cell, there be no risk of electrodes short-circuiting at the time of energization, etc. When it considers at such a thing, as sum total thickness after the second layer, 5 micrometers or more are required and its 10 micrometers or more are still more desirable.
[0021] As a solution containing an ion-exchange-resin component used for this invention, if a fluorine system ion-exchange-resin component is included, it is desirable that it is the polymer which has the following chemical formula, for example anything although it is good.
[0022]
[Formula 1]

$$-[(CF_2-CF_2)_i-(CF_2-\underset{\underset{\displaystyle \underset{\displaystyle CF_3}{\overset{|}{(OCF_2-CF)_x}}-O-(CF_2)_y-SO_3H}{|}}{CF})_j]_n-$$

(式中$x=0\sim2$；$y=2\sim3$；$i/j=0\sim10$)

[0023] Since the equivalent weight of an ion-exchange-resin component has problems, like reinforcement becomes weak when it is too small to remainder although it is so good that it is small from an electric resistance side, its 1100 g/eq - 600 g/eq is desirable practical. Although especially the solvent of the solution containing an ion-exchange-resin component is not limited, the mixed solvent which added water, for example to isopropanol, propanol, ethanol, a methanol, etc. can be used for it.
[0024] And it shows it. [drawing 1] [the zygote of this invention] [**] [type] In drawing 1 , the gas diffusion electrode 1 consists of a hydrophobing layer 2 and an electrode catalyst bed 3, and the solid-state polyelectrolyte layer first pass 4 is formed even in the front face from the interior of the electrode catalyst bed 3. On the solid-state polyelectrolyte layer first pass 4, 5 is formed two layer of solid-state polyelectrolyte ****, and 6 is further formed the third layer of a solid-state quantity molecular layer on it. There is an electrode catalyst particle 8 supported on carbon 7 in the electrode catalyst bed 3, and coating of the solid-state polyelectrolyte layer first pass 4 is carried out on it.
[0025] The solid-state macromolecule layer first pass has also covered the carbon 7 top with which the part sank in in the electrode catalyst bed 3, and the electrode catalyst particle 8 was supported. There is a hole 9 in the electrode catalyst bed 3, and gas is supplied to the electrode catalyst 8 by this hole 9. The solid-state polyelectrolyte layer first pass 4 needs to be the thickness of extent which blockades the hole 9 in the electrode catalyst bed 3, and does not check circulation of gas. For this reason, in case two layer of solid-state polyelectrolyte **** or subsequent ones are applied, it is important for the solid-state polyelectrolyte layer first pass to dissolve again, or for a solid-state polyelectrolyte component to sink in through the first pass, and to make this hole small or to make it not blockade. If the first pass is formed by the approach of this invention, since it does not happen, such a thing can constitute a highly efficient fuel cell.
[0026] In case a fuel cell is constituted using the zygote of the solid-state polyelectrolyte layer and electrode like drawing 1 , the electrode which has a solid-state polyelectrolyte layer more than a bilayer, and another side have the approach of making stick the sides which have the layer of a solid-state polyelectrolyte for the electrode which has only the first pass, and carrying out heat press junction, and the desirable approach of joining similarly electrodes with the solid-state polyelectrolyte layer more than a bilayer. The junction to the electrode which has a solid-state polyelectrolyte layer more than a bilayer in one electrode, and an electrode without such a layer is [an inclination for adhesion with an electrode to worsen and for electric resistance to become high] and is not desirable.
[0027] As for the temperature at the time of joining the electrode which has a solid-state polyelectrolyte layer, it is desirable that it is the temperature to which a solid-state

polyelectrolyte becomes to some extent soft, and it is desirable for usually obtaining 120 degrees C or more and good adhesion. [of 140 degrees C or more] The pressure at the time of joining is not limited especially that what is necessary is just to decide on the pressure which good adhesion tends to obtain to virtual junction temperature. Thus, if a fuel cell is constituted using the zygote of the solid-state polyelectrolyte layer and electrode which were obtained by the creation approach of this invention and the electrical and electric equipment is taken out for oxygen gas and hydrogen gas in a raw material, a fuel cell output higher than the case where a conventional electrode and a conventional ion-exchange-membrane zygote are used will be obtained, and the stability will not be different from the conventional thing, either.
[0028] When this invention creates the zygote of the solid-state polyelectrolyte for fuel cells, and an electrode in this way, The first pass is formed by applying and heat-treating on an electrode the solution of the fluorine system polymer which contains a sulfonic group for the layer used as a polyelectrolyte at the side which has an electrode catalyst. Furthermore, since it is formed by making the layer after the second layer form by applying the fluorine system polymer solution containing a sulfonic group on the first pass The layer of a solid-state polyelectrolyte can be made thin, the electric resistance of a junction interface or a solid-state polyelectrolyte layer and mass transfer resistance are excellent in small adhesion, and a fuel cell with a large output can be constituted.
[0029] Next, although an example explains this invention, it is not limited to this.
[0030]
[Example]
[0031]
[Example 1] The solution A containing 5 % of the weight of ion-exchange-resin components which are the equivalent weight of 1000g / solid-state polyelectrolyte of eq shown in the following-ization 2 was prepared.
[0032]
[Formula 2]

[0033] The presentation of Solution A shall contain the propyl alcohol 85 section, the water 10 section, and the ion-exchange-resin component 5 section. as the gas diffusion electrode for fuel cells -- the size 3cmx3cm product made from E-TEK -- a platinum catalyst -- 0.35 mg/cm2 it is -- two things were prepared. It applied 117mg of solutions A to the catalyst side of this electrode of two sheets at a time, and it was made to dry them at the temperature of 40 degrees C for about 1 hour. It heat-treated for 10 minutes within hot air drying equipment with a temperature of 140 degrees C further after that, and the first pass was formed. After making the first pass form,

applied the 117mg solution A, and it was made to dry at 40 degrees C for 1 hour, and heat-treated for 10 minutes within 140 more-degree C hot air drying equipment, and the second layer was made to form on the first pass of an electrode of two sheets. After making the second layer form, even the third layer, the fourth layer, and the fifth layer were formed by the same approach as the second layer.

[0034] Next, the spreading layer sides of this electrode of two sheets are stuck, and they are 145 degrees C and 60kg/cm2 with heat press equipment. The heat press was carried out for 90 seconds on conditions, and Zygote B was obtained. Thus, the thickness of a solid-state polyelectrolyte layer was about 20 micrometers, the junction condition was also firm and the created zygote B did not exfoliate simply. It equipped between 2cm and the 3cm x3cm flanges of inside dimension [of 2cm] x outside ** which are made to stick the electric supply object for taking out the electrical and electric equipment for this zygote B on those both sides, and have the intake and draw opening of gas, and the body of a fuel cell was constituted. The fuel cell was connected to the external load, and the output current and output voltage were measured on condition that 55 degrees C and 1atm, having supplied hydrogen gas to one side and supplying oxygen gas to another side. The result is shown in drawing 2 .

[0035]

[The example 1 of a comparison] The completely same solution A as an example 1 and the gas diffusion electrode were prepared. Moreover, Nafion 117 of DuPont which is the ion exchange membrane of the sulfonic acid type of a fluorine system as ion exchange membrane was also doubled and prepared. The two same electrodes as an example 1 were prepared, and the first pass was formed on the completely same conditions as an example 1 except not heat-treating at 140 degrees C.

[0036] Ion exchange membrane was beforehand processed by 100 degrees C of sulfuric acids 8% for 2 hours, and after pure water washed after that, it was immersed into the pure water boiled for about 1 hour. After wiping off the waterdrop of the front face of ion exchange membrane, the spreading side of the electrode of two sheets is turned and stuck to an ion-exchange-membrane side, and they are 145 degrees C and 60kg/cm2 with heat press equipment. The heat press was carried out for 90 seconds on conditions, and Zygote C was obtained.

[0037] The fuel cell was constituted for this zygote C completely like the example 1, and the engine performance was measured. A result is shown in drawing 2 . As for the zygote of the solid-state polyelectrolyte layer for fuel cells and electrode which were created by this invention approach, it is clear that the fuel cell engine performance is good.

[0038]

[Effect of the Invention] Since a solid-state polyelectrolyte layer can be thinly formed by the manufacture approach of this invention in case the zygote of the solid-state polyelectrolyte for fuel cells and an electrode is manufactured, the electric resistance of a solid-state polyelectrolyte layer and mass transfer resistance can constitute the fuel cell with a large output which was excellent in small adhesion.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] They are the sectional view in which, and having shown it, and its partial enlarged drawing. [the zygote of the solid-state polyelectrolyte of this invention, and an electrode] [**] [type]
[Drawing 2] It is the graphical representation having shown the output current of the solid-state polyelectrolyte fuel cell of the example 1 of this invention, and the example 1 of a comparison, and the property of output voltage.
[Description of Notations]
1 Gas Diffusion Electrode
2 Hydrophobing Layer
3 Electrode Catalyst Bed
4 Solid-state Polyelectrolyte Layer First Pass
5 Two Layer of Solid-state Polyelectrolyte ****
6 Three Layer of Solid-state Polyelectrolyte ****
7 Carbon
8 Electrode Catalyst Particle
9 Hole

[Translation done.]